

Hydrogen-Treated α -Fe₂O₃ Nanorods for Solar Water Splitting

Haiqing Ma¹, Mahadeo A. Mahadik¹, Jin Woo Park¹, Manish Kumar², Hee Suk Chung³,
Weon Sik Chae⁴, Hyun Hee Lee², Sun Hee Choi², and Jum Suk Jang¹

¹ Division of Biotechnology, Advanced Institute of Environmental and Bioscience, College of Environmental and Biore-source Sciences, Chonbuk National University, Iksan 570-752, Republic of Korea

Phone: +82-63-850-0846 E-mail: jangjs75@jbnu.ac.kr

² Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH),
Pohang 37673, Republic of Korea

³ Korea Basic Science Institute, Jeonju Center Jeonju 54907, Republic of Korea

⁴ Korea Basic Science Institute, Daegu Center, Daegu 41566, Republic of Korea

Abstract

In this study, we present an advanced strategy of the low temperature hydrogen annealing combined with high temperature quenching for activating β -FeOOH to improve the photoelectrochemical performance of hematite photoanodes. Hydrogen-treated α -Fe₂O₃ nanorods were prepared by annealing β -FeOOH in hydrogen atmosphere at 360°C followed by high temperature quenching. The obtained α -Fe₂O₃ photoanode shows a substantially enhanced photocurrent density of 1.35 mA/cm² at 1.23 V_{RHE}, which is approximately 70% higher than directly quenched α -Fe₂O₃ photoanode. The incorporation of Sn dopants from the FTO substrates in the hematite lattice and the forming of oxygen vacancies were confirmed by X-ray photoelectron spectroscopy.

1. Introduction

Photoelectrochemical (PEC) hydrogen production by solar water splitting is one of the most studied methods to convert solar energy to clean hydrogen fuel for solving the energy and environmental crisis. Hematite (α -Fe₂O₃) is an earth abundant, chemically stable and low cost material, with a suitable band gap for efficient visible light absorption in a photoelectrochemical cell.¹⁾ However, there are factors limiting the performance of hematite including large required overpotential, low absorption coefficient, short hole diffusion length (2~4 nm), slow water oxidation kinetics and poor conductivity.^{2,3)} Great efforts have been devoted to overcome these limitations such as nano-structuring and elemental doping. One-dimensional α -Fe₂O₃ nanostructures (e.g., nanorods, nanotubes, etc.), can effectively reduce short hole diffusion. Doping with metal atoms (e.g., Ti, Zr, and Sn, etc.) can significantly improve the electronic conductivity of α -Fe₂O₃.^{4,5)}

Recently, Sn doping has been shown to improve the PEC performance of hematite photoanodes, by surface treatment or/and by self-Sn diffusion doping from the underlying fluorine doped SnO₂ (FTO) substrates.⁶⁾ Moreover, introduction of oxygen vacancies (Fe²⁺) within the hematite crystal structure by controlled annealing under an oxygen-deficient atmosphere has been reported as a way to activate the α -Fe₂O₃ photoanode for solar water splitting.⁷⁾ In this study, we presented an effective method by simply using H₂ treatment during the thermal annealing process to

boost the PEC performance of α -Fe₂O₃ photoanode.

2. Results and Discussion

β -FeOOH nanorods on FTO substrates were prepared by a simple hydrothermal method as reported by Vayssieres et al.⁸⁾ The as-synthesized β -FeOOH thin films were annealed in a tube furnace at 360°C for 1 h with a hydrogen flow rate of 100 mL/min, denoted as H360. The hydrogen reduced films were subsequently subjected to high temperature quenching in ambient air (800°C for 10 min), denoted as H360A800. A control sample only quenching β -FeOOH at 800°C for 10 min was also prepared, denoted as A800.

The β -FeOOH nanorods show the characteristic doublet (Fe2p_{3/2} and Fe2p_{1/2}) peaks at 711.0 and 724.9 eV in Fig. 1a. In addition, the Fe2p_{3/2} satellite peak (octahedral Fe³⁺) of the β -FeOOH sample appears at 719 eV. After hydrogen reduction, this particular peak position shifts to 716 eV, indicating the presence of a characteristic of Fe²⁺ in the octahedral site of the magnetite phase (Fe₃O₄). This confirms the phase transformation from β -FeOOH to Fe₃O₄ by the hydrogen annealing for the sample H360. After high temperature quenching of H360, the presence of satellite peaks at approximately 719 and 716 eV were observed, suggesting that Fe²⁺ is oxidized to Fe³⁺ and the presence of Fe²⁺ species (oxygen vacancies) is retaining in high temperature quenched sample H360A800. As shown in Fig. 1b XPS Sn3d spectra, H360, A800, and H360A800 all exhibit peaks centered at 486.5 eV and 494.5 eV, corresponding to binding energies of Sn3d_{5/2} and Sn3d_{3/2}, respectively. It is suggested that the iron oxides are substitutionally doped by Sn⁴⁺ ions. Also, the intensity of the Sn3d XPS peak increased with hydrogen annealing which indicates an increasing amount of diffused Sn content from FTO substrates. The Sn content in hydrogen-treated α -Fe₂O₃ photoanode H360A800 is higher than in directly quenched hematite nanorods (A800).

The α -Fe₂O₃ nanorods H360A800 grow along the (110) direction in single crystalline structure as is shown in the TEM images (Fig. 1c). The width of H360A800 nanorods is about 55 nm. The corresponding elemental mapping images show that all of the Fe, O, and Sn elements were uniformly distributed in the H360A800 sample.

In Fig. 1d, the directly quenched hematite photoanode

A800 shows a photocurrent density of 0.80 mA/cm² at 1.23 V_{RHE}. The PEC performance was dramatically improved with hydrogen annealing followed by high temperature quenching, owing to the unexpected Sn⁴⁺ diffusion on the surface and doping into the hematite lattice. Thus, H360A800 photoanode shows a photocurrent density of 1.35 mA/cm² at 1.23 V_{RHE} which is 70% larger than that of A800.

Fig. 1e shows PL (photoluminescence) decays of A800 and H360A800 samples. H360A800 shows longer lifetime components as compared to A800. This result indicates that H360A800 with a little retarded electron-hole recombination lifetime provides somewhat more charge separation environment.

A schematic diagram is presented in Fig. 1f. Directly high temperature quenching leads to the lower Sn⁴⁺ doping into the α -Fe₂O₃ nanorods (A800). The thermal reduction of Hydrogen annealing of β -FeOOH at 360 °C results in the formation of magnetite (Fe₃O₄) and increases the unexpected Sn⁴⁺ diffusion from FTO substrates. Further, the following high temperature quenching oxidizes Fe₃O₄ into hematite (α -Fe₂O₃) and induces more Sn⁴⁺ doping into its crystal lattice as conformed by XPS analyses.

3. Conclusions

In summary, hydrogen treated hematite photoanode was investigated as a means for efficient PEC water splitting. Hydrogen annealing greatly influences the performance of hematite nanorods grown on FTO substrates, due to the introducing of oxygen vacancies and high concentration of

Sn⁴⁺ self-doping in the photoanode. The hydrogen treated hematite photoanode showed 80% increase in photoactivity over that of β -FeOOH directly quenched at 800°C. This work develops a simple strategy to introduce self-doped Sn⁴⁺ as well as oxygen vacancies for the promotion of water splitting efficiency.

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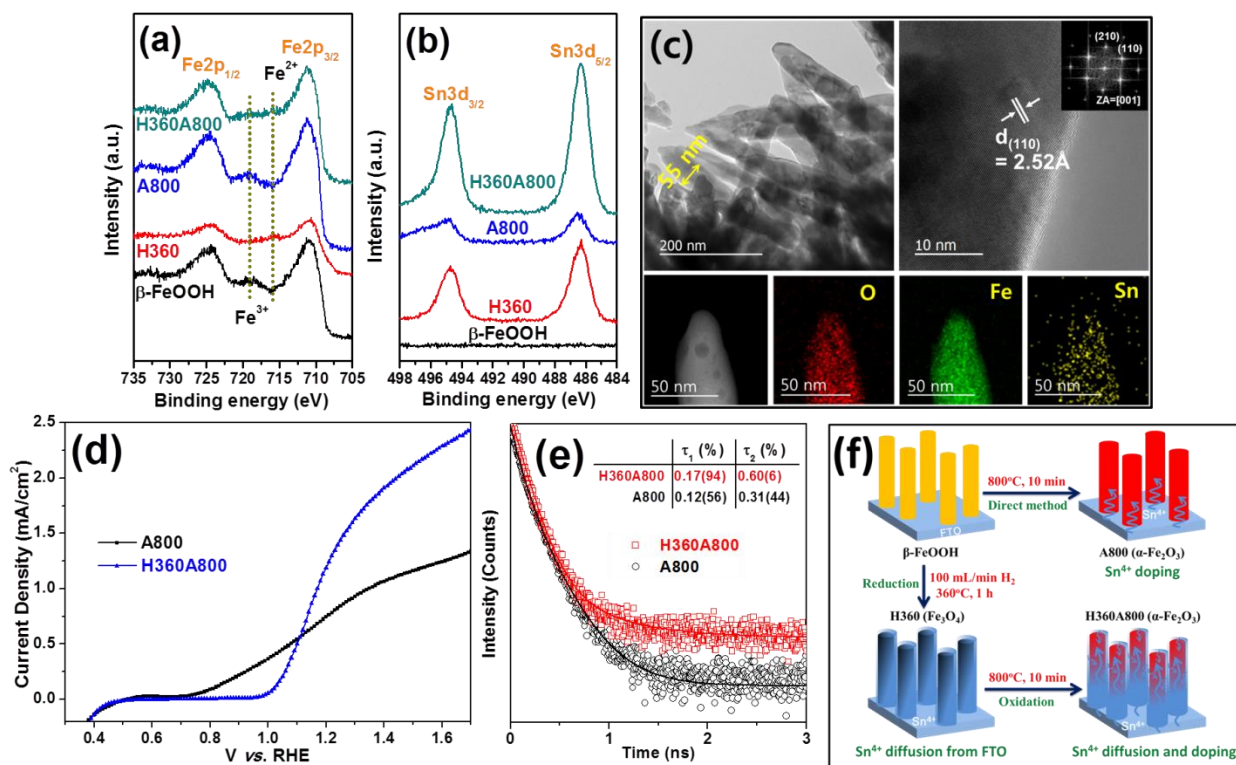


Fig. 1 (a) Fe2p XPS spectra. The dashed lines in (a) highlight the satellite peaks of Fe³⁺ and Fe²⁺ species. (b) Sn3d XPS spectra. (c) TEM and EDS elemental mapping images of H360. (d) Photocurrent density-voltage curves of A800 and H360A800. (e) PL decays of A800 and H360A800. The solid lines are fitted curves. Inset is the PL lifetime parameters of the corresponding PL decays. (f) Schematic diagram of hydrogen assisted thermal activation of hematite.